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Final Technical Report on NASA Contract NAS 9-11827

by

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Adsorption Bed Models Used in Simulation of Atmospheric Control Systems

The last segment of this contract involved the study of trace contaminant capacity of HSC adsorbent. Two separate techniques were used to obtain important basic data for the adsorption of seven liquid and eight gaseous trace contaminants. The volumetric system used by L. D. Kissinger in previous HSC studies was modified to determine the HSC capacity of all the contaminants. This apparatus was restricted to determinations at much higher contaminant concentrations than are likely to be encountered in spacecraft. A second study of six of the liquids was carried out in a gas chromatograph (Antek 300). The latter studies report data for gas concentrations in the ppm range and should be quite accurate for the compounds studied. The advantage of the chromatographic system is the extreme sensitivity of the detector to very low concentrations of hydrocarbons and alcohols. Unfortunately the detector responds erratically to Freon-11 and not at all to ammonia so these compounds could not be studied.

The results of these studies are reported in two parts. First a brief summary of the chromatographic results are given as an attachment to this report. Second, the thesis of Mr. Dennis Yieh reports in some detail the results of his volumetric studies. Comparisons of the data that are common to both studies are also included in the attachment.

Chromatographic Study of Trace Contaminants on HSC

Theory

Gas chromatographic systems consist of a gas source, sample injector, packed column and detector. A carrier gas flows continually through the column. A small amount of sample is injected into the carrier gas and the elements in the sample observed as they pass through the detector. The purpose may be to determine the composition of the sample. This is done by selecting a packing that will separate the components in the sample. The system may also be used to determine the interaction of the material in the sample with the packing. This was the purpose of these studies.

In an ideal packed column with uniform flow, negligible diffusion and no resistance to transfer of material between the gas and solid a mass balance for any component A is

1) $$q \frac{\partial C_A}{\partial z} + \rho A \frac{\partial W}{\partial t} = 0$$

q is the gas flow rate cc/min

C_A is the gas concentration mols/cc

ρ is the packing density g/cc of bed

A is the bed cross section

W is the solid loading g_A / g_{solid}

For low concentrations

2) $$\frac{P_A}{W} = \mathcal{P}_A$$

Where P_A is the partial pressure of A in the gas (mmHg)

and $\mathcal{P}_A$ is a partition coefficient (mmHg)

Then for ideal gases

3) $C_A = P_A/RT$

Where R is the gas constant (62, 360 in consistant units) and T is the absolute temperature ^{o}K

Combining 1, 2 and 3 gives

4) $\frac{q}{RT} \frac{\partial P_A}{\partial z} \frac{\rho A}{\mathcal{P}_A} \frac{\partial P_A}{\partial t} = 0$

The peak of an impulse in concentration of A satisfies

5) $dP_A = 0 = \frac{\partial P_A}{\partial z} dz + \frac{\partial P_A}{\partial t} dt$

The velocity of such a peak is $\frac{dz}{dt} = V$

Thus 4 and 5 are consistant only if

6) $V = \frac{q\mathcal{P}_A}{A\rho RT} = \frac{L}{t}$

Where L is the length of the bed and t is the time required for the peak to traverse the bed. This allows us to determine the partition coefficient as

7) $\mathcal{P}_A = \frac{(AL\rho)\,RT}{qt} = \frac{mRT}{qt}$

Where m is the mass of absorbent in the bed

Even if diffusion occurs in the gas the relation given by 7 remains valid if the bed is very long and t is the time required for the highest concentration of A to be after injection.

Experimental Procedure

An Antek 300 chromatograph with dual flame ionization detectors was used in the study. Two columns were packed with HSC. Each was 1 mm ID by about 40 cm long. The column designated A contained 0.563 g HSC while B had 0.606 g HSC in it. The signal from the detectors was recorded on a Linear Instruments Corporation Recorder.

With the flow regulators on the GC fixed the flow through the beds was found to vary almost linearly with the regulator (on the gas bottle) pressure. The flow through each column was determined both before and after the series of tests reported and is given below for test conditions

Bed/Reg. P (psi)	60	80	90
A	55 cc/min	72 cc/min	78 cc/min
B	81 cc/min	104 cc/min	116 cc/min

Three series of tests were conducted. In the first nitrogen was the carrier and the beds were maintained at 50°C (minimum that can be achieved under normal isothermal operation).

An almost duplicate set of runs made up the second series but N_2 with 1% CO_2 was used as the carrier. In the third sequence the door of the oven was left open during the runs so that the bed temperatures could be kept close to 25°C.

The time required for a sample to be detected in an empty tube with flow rates comparable to those in the test was found to be less than 5 seconds. Thus since measured residence times were in excess of 5 minutes the dead space

was ignored.

During each run the regulator pressure was set and adjusted occasionally to keep it at a desired value. The bed temperature was monitored and kept close to a desired value by manually turning the heaters on or off. The heaters on the injector ports and at the detectors were found to cause the oven temperature to reach 50°C even with the oven heater off. A sample was injected and the time required for the measured outlet concentration to peak determined by use of a digital watch in short runs or by measuring the distance on the recorder in some long runs. These times are listed in Table I.

Table I

Peak Times Observed in Chromatographic Runs

Run	Bed	Component	time (hr: min: sec)
	Series I	N_2 carrier gas	Reg P = 80 psi T = 51°C
1	A	1% methanol in water	7:09
2	B	"	5:17
3	A	1% ethanol in water	21:05
4	B	1% methylacetate in water	15:27
5	A	benzene	43:56
6	B	Toluene	2:48:00
7	A	Isobutanol	3:32:00
8	A	1% methanol in water	6:59
	Series II	N_2 = 1% CO_2 carrier gas	Reg P = 80 psi T = 51°C
9	A	1% MeOH	6:35
10	B	1% MeOH	4:56
11	A	1% E+OH	23:45
12	B	1% MeAc	17:31
13	A	Benzene	42:00
14	B	Toluene	2:43:00
	Series III	N_2 carrier gas	Reg P - 90 psi T = 24°C
15	A	1% MeOH	33:57
16	B	1% MeOH	26:00
17	A	1% E+OH	2:16:00
18	B	1% MeAc	2:00:30

Calculated Results

Equation 7 was used to determine partition coefficients for each case reported. These results are given as Table II. Included in this are estimates of the coefficients for each of the liquids studied by Yieh. The methanol data fits almost perfectly but the more strongly adsorbed compounds show considerable deviation. These differences could be caused by the long residence time needed to collect such data on the chromatograph (this invalidity take ideal bed assumptions) or the very non-linear isotherms of the components leading to difficulties in extrapolating Yieh's data to low concentrations.

Conclusions

Table II shows clearly that preadsorbed CO_2 has little effect on the capacity of HSC for the liquid trace contaminants. Thermal effects are very pronounced. The chromatographic results agree quite well with the volumetric results of Yieh.

Table II

Partition Coefficients for Trace Contaminants
Partial Pressure in Gas/(wt. Adsorbed/ wt. HSC) mmHg

	No CO_2	Preadsorbed		Gas in Eqil with 7 mmHg CO_2
Component	T = 24°C	25°C	51°C	T = 51°C
Freon-11		68		
Methanol	116-123	130	693-759	756-813
Methyl Acetate	10.9	17.5	103	90.5
Ethanol	21.4		146	131
Acetone		34		
Benzene		12.5	46.5	48.6
Toluene		small	7.8	8.0
Isobutanol		small	10.2	

Summary of Work Performed Under NAS 9-11827

May 7, 1971 - December 31, 1978

"Adsorption Bed Models Used in Simulation of Atmospheric Control Systems"

Three classes of adsorbents were studied under this contract. The initial contract was written to study coadsorption phenomena in molecular sieve beds. The results of this study were reported in the Ph. D. thesis of Dr. Glenn G. Bernard[1] and the M.S. thesis of Mr. Yun-Tak Lee[2].

In a first extension of the contract the adsorption properties of potassium superoxide were studied. The results of this experimental study were submitted in a final report on the study in 1977[3]. These results were summarized in papers[4, 5] presented at Intersociety Conferences on Environmental Control Systems in 1974 and 1977.

In a second extension of the contract the adsorption of CO_2 and H_2O by HSC adsorbent was studied. The results of this work was reported in the M.S. thesis of Mr. Lawrence D. Kissinger[6]. A summary of the work was presented at the 1977 Intersociety Conference on Environmental Systems[7].

The third extension of the contract allowed the final set of data on trace contaminant capacity of HSC to be collected. This final report and the M.S. thesis of Mr. Dennis T. Yieh[8] give the results of this last extension.

References

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3) Davis, S.H. "Final report on Adsorption Bed Models Used in Simulation of Atmospheric Control Systems: Potassium Superoxide Study", May, 1977.

4) Davis, S. H. and Blakemore, T. L. "Modeling of Absorbent and Oxygen Supply Systems", Intersociety Conference on Environmental Control Systems, Seattle, Washington, July, 1974.

5) Davis, S.H. "KO_2 Reactions with CO_2 and H_2O in Air", Intersociety Conference on Environmental Systems, San Francisco, California, July, 1977.

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8) Yieh, Dennis T. "Trace Contaminant Studies of HSC Adsorbent" M.S. Thesis, Rice University, May, 1979.